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Untangling the Energetics and Dynamics of Boron Monoxide Radical Reactions

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Untangling the Energetics and Dynamics of Elementary Reactions of the Boron Monoxide Radical (^{11}BO ; $X^2\Sigma^+$)

Final Report - Grant FA9550-12-1-0213

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1. Objectives

The objectives of this project are to experimentally explore the energetics, dynamics, and potential energy surfaces (PESs) of elementary reactions of ground state boron monoxide radicals (^{11}BO ; $\text{X}^2\Sigma^+$) with key C2 to C6 unsaturated hydrocarbons under single collision conditions utilizing a crossed molecular beams machine. The experiments employ a hydrocarbon-free crossed molecular beams machine with ultra-sensitive detection schemes incorporating a universal, rotatable angular resolved time-of-flight (TOF) mass spectrometric detector with electron impact ionization as well as laser induced fluorescence (LIF) detection. By conducting state-of-the-art crossed molecular beam experiments and combining these results with electronic structure calculations in collaboration with Profs. Bartlett (University of Florida), Mebel (Florida International University), and Chang (National Dong Hwa University, Taiwan), we extract the chemical dynamics, reaction mechanisms, products, intermediates, energetics, branching ratios, and enthalpies of formation of small carbon-, hydrogen, oxygen-, and boron-bearing (CHOB) molecules. The proposed studies are of fundamental interest to the fields of boron combustion chemistry, boron-based chemical propulsion systems, and to the physical-organic chemistry community to advance insights into basic chemical structure and chemical bonding of carbon-, hydrogen-, oxygen-, and boron-bearing molecules (CHOB molecules).

2. Relevance to AFOSR Sponsored Research

This proposed research is in line with the strategic plan of AFOSR's *Aerospace, Chemistry, and Material Sciences* directorate and its *Molecular Dynamics* program. The objectives of this program are to understand, predict, and control the chemical reactivity and flow of energy in molecules. These data are of importance to understand the chemistry in rocket and aircraft propulsion systems where predictive capabilities and control of chemical reactivity and energy flow at a detailed molecular level is of crucial importance. Further, our studies assist to developing a basic understanding and predictive capabilities for chemical reactivity, bonding, and energy transfer processes are also encouraged, here the reactivity of open shell radicals (boron monoxide) and of the isoelectronic cyano radical with hydrocarbon molecules which serve as prototype reaction partners of alkenes, alkynes, and aromatic systems. Our data can be utilized to understand chemical propulsion systems and the elementary steps of radical reactions as well as the unimolecular decomposition of open shell species on the molecular level. Due to the collaborations with theoreticians (Bartlett/Mebel/Chang), our research holds also strong links to the *Theoretical Chemistry* program. Further, one of the prime interests of the AFOSR is to sponsor combustion related research which provides data and procedures to enable the development of reliable chemical propulsion systems to quantitatively predict the performance of combustion and propellant systems to minimize the emission of unwanted by-products and to maximize the propulsion efficiency. However, all combustion models require crucial input parameters such as the knowledge of rate constants of the chemical reactions over a wide temperature and pressure range, the identification of reaction intermediates, which either form products, are stabilized via three body reactions, react with other molecules, or decay back to the reactants, and the assignment of the primary reaction products together with branching ratios. At present this includes AFOSR sponsored research to understand, predict, and to control rocket propulsion systems and the reactivity, energy flow in molecular systems, an also the interest in steady state plasmas. Our research initiative connects to the *Combustion and Diagnostics* and *Space Power and Propulsion* programs aimed to untangle the chemistry of reacting flows of chemical propulsion systems in chemical rockets and ramjet engines. Based on these data, the ultimate goal is to predict and to eliminate combustion instabilities, to minimize the emission of unwanted by-products, and to optimize the efficiency of chemically-based propulsion systems.

3. Accomplishments

3.1. Crossed Beam Reactions of Boron Monoxide with Acetylene and Ethylene (P1, P8)

The reaction dynamics of boron monoxide ($\text{BO}; X^2\Sigma^+$) with acetylene ($\text{C}_2\text{H}_2; X^1\Sigma_g^+$) and with ethylene ($\text{C}_2\text{H}_4; X^1A_g$) were investigated under single collision conditions at collision energy of 12 to 13 kJ mol^{-1} employing the crossed molecular beam technique; electronic structure RRKM calculations were conducted to complement the experimental data. The reactions were found to have no entrance barrier and proceeded via indirect scattering dynamics initiated by an addition of the boron monoxide radical with its boron atom to the carbon-carbon triple and double bond, respectively, forming the $\text{O}^{11}\text{BHCCH}$ and $\text{O}^{11}\text{BH}_2\text{CCH}_2$ intermediates. The latter either decomposed via hydrogen atom emission to form the ethynyl boron monoxide (HCCBO) and vinylboron monoxide products ($\text{C}_2\text{H}_3\text{BO}$) through tight exit transition states. An alternative channel, which was found to have a lower significance, involved a hydrogen migration in the initial collision complexes to form $\text{O}^{11}\text{BCCH}_2$ and $\text{O}^{11}\text{BHCCH}_3$ radical intermediates, respectively, which in turn can also emit atomic hydrogen. The overall reaction energies to form thynyl boron monoxide (HCCBO) and vinylboron monoxide products ($\text{C}_2\text{H}_3\text{BO}$) were determined to be $62 \pm 8 \text{ kJ mol}^{-1}$ and $40 \pm 10 \text{ kJ mol}^{-1}$, respectively.

3.2. Crossed Beam Reaction of Boron Monoxide with Diacetylene (P4)

The reaction dynamics of the boron monoxide radical ($^{11}\text{BO}; X^2\Sigma^+$) with diacetylene ($\text{C}_4\text{H}_2; X^1\Sigma_g^+$) were investigated at a nominal collision energy of 17.5 kJ mol^{-1} employing the crossed molecular beam technique and supported by *ab initio* and statistical (RRKM) calculations. The reaction is governed by indirect (complex forming) scattering dynamics with the boron monoxide radical adding with its boron atom to the carbon-carbon triple bond of the diacetylene molecule at one of the terminal carbon atoms without entrance barrier. This leads to a doublet radical intermediate ($\text{C}_4\text{H}_2^{11}\text{BO}$), which undergoes unimolecular decomposition through hydrogen atom emission from the C1 carbon atom via a tight exit transition state located about 18 kJ mol^{-1} above the separated products. This process forms the hitherto elusive boronyldiacetylene molecule ($\text{HCCCC}^{11}\text{BO}; X^1\Sigma^+$) in a bimolecular gas phase reaction under single collision conditions. The overall reaction was determined to be exoergic by 62 kJ mol^{-1} . The reaction dynamics are compared to the isoelectronic diacetylene ($\text{C}_4\text{H}_2; X^1\Sigma_g^+$) – cyano radical ($\text{CN}; X^2\Sigma^+$) system studied previously in our group. The characteristics of boronyl-diacetylene and the boronyldiacetylene molecule ($\text{HCCCC}^{11}\text{BO}; X^1\Sigma^+$) as well as numerous intermediates are reported for the first time.

3.3. Crossed Beam Reaction of Boron Monoxide with Methylacetylene (P5)

The crossed molecular beam reaction of boron monoxide ($^{11}\text{BO}; X^2\Sigma^+$) with methylacetylene ($\text{CH}_3\text{CCH}; X^1A_1$) was investigated at a collision energy of 22.7 kJ mol^{-1} . The scattering dynamics were found to be indirect (complex forming reaction) and were initiated by the addition of $^{11}\text{BO}(X^2\Sigma^+)$ to the π electron density at the acetylenic carbon-carbon triple bond without an entrance barrier. The resulting $^{11}\text{BOC}_3\text{H}_4$ doublet radical intermediates underwent unimolecular decomposition involving three competing reaction mechanisms via two distinct atomic hydrogen losses and a methyl group elimination. Utilizing partially deuterated methylacetylene reactants ($\text{CD}_3\text{CCH}; \text{CH}_3\text{CCD}$), we revealed that the initial addition of $^{11}\text{BO}(X^2\Sigma^+)$ to the C1 carbon atom of methylacetylene was followed by hydrogen loss from the acetylenic carbon atom (C1) and from the methyl group (C3) leading to 1-propynyl boron monoxide ($\text{CH}_3\text{CC}^{11}\text{BO}$) and propadienyl boron monoxide ($\text{CH}_2\text{CCH}^{11}\text{BO}$), respectively. Addition of $^{11}\text{BO}(X^2\Sigma^+)$ to the C1 of methylacetylene followed by the migration of the boronyl group to the C2 carbon atom and/or an initial addition of $^{11}\text{BO}(X^2\Sigma^+)$ to the sterically less accessible C2 carbon atom of methylacetylene was followed by

loss of a methyl group leading to the ethynyl boron monoxide product (HCC^{11}BO) in an overall exoergic reaction ($78 \pm 23 \text{ kJ mol}^{-1}$). The branching ratios of these channels forming $\text{CH}_2\text{CCH}^{11}\text{BO}$, $\text{CH}_3\text{CC}^{11}\text{BO}$, and HCC^{11}BO were derived to be $4 \pm 3\%$, $40 \pm 5\%$, $56 \pm 15\%$, respectively; these data are in excellent agreement with the calculated branching ratios using statistical RRKM theory yielding 1 %, 38 %, and 61 %, respectively.

3.4. Crossed Beam Reaction of Boron Monoxide with Benzene (P6)

Organyl oxaboranes (RBO) are valuable reagents in organic synthesis due to their role in Suzuki coupling reactions. However, organyl oxaboranes (RBO) are only found in trimeric forms (RBO_3) commonly known as boronic acids or boroxins; obtaining their monomers has proved a complex endeavor. Here, we demonstrate for the first time an oligomerization-free formation of organyl oxaborane (RBO) monomers in the gas phase by a radical substitution reaction under single collision conditions in the gas phase. Using the cross molecular beams technique, phenyl oxaborane ($\text{C}_6\text{H}_5\text{BO}$) is formed through the reaction of boronyl radicals (BO) with benzene (C_6H_6). The reaction is indirect, initially forming of a van-der-Waals complex that isomerizes below the energy of the reactants, eventually forming phenyl oxaborane by hydrogen emission in an overall exoergic radical - hydrogen atom exchange mechanism.

3.5. Crossed Beam Reaction of Boron Monoxide with Dimethylacetylene (P7)

The crossed molecular beam reaction of boron monoxide ($^{11}\text{BO}; \text{X}^2\Sigma^+$) with dimethylacetylene ($\text{CH}_3\text{CCCH}_3; \text{X}^1\text{A}_{1g}$) was investigated at a collision energy of $23.9 \pm 1.5 \text{ kJ mol}^{-1}$. The scattering dynamics were suggested to be indirect (complex forming reaction) and were initiated by the addition of $^{11}\text{BO}(\text{X}^2\Sigma^+)$ with the radical center located at the boron atom to the π electron density at the acetylenic carbon-carbon triple bond without entrance barrier leading to cis/trans $^{11}\text{BOC}_4\text{H}_6$ doublet radical intermediates. Cis $^{11}\text{BOC}_4\text{H}_6$ underwent cis-trans isomerization followed by unimolecular decomposition via a methyl group (CH_3) loss forming 1-propynyl boron monoxide ($\text{CH}_3\text{CC}^{11}\text{BO}$) in an overall exoergic reaction (experimental: $-91 \pm 22 \text{ kJ mol}^{-1}$; theoretical: $-105 \pm 9 \text{ kJ mol}^{-1}$; NIST: $-104 \pm 12 \text{ kJ mol}^{-1}$) via a tight exit transition state; trans $^{11}\text{BOC}_4\text{H}_6$ was found to emit a methyl group instantaneously. Neither atomic nor molecular hydrogen loss pathways were detectable. The experimental finding of an exclusive methyl loss pathway gains full support from our computational study predicting a methyl group versus atomic hydrogen loss branching ratio of 99.99 % to 0.01 % forming 1-propynyl boron monoxide ($\text{CH}_3\text{CC}^{11}\text{BO}$) and 1-methyl-propadienyl boron monoxide ($\text{CH}_3(^{11}\text{BO})\text{CCCH}_2$), respectively.

3.6. Crossed Beam Reaction of Boron Monoxide with Allene (P9)

The gas phase reaction between the boron monoxide radical ($^{11}\text{BO}; \text{X}^2\Sigma^+$) and allene ($\text{H}_2\text{CCCH}_2; \text{X}^1\text{A}_1$) was investigated experimentally under single collision conditions using the crossed molecular beam technique and theoretically exploiting *ab initio* electronic structure and statistical (RRKM) calculations. The reaction was found to follow indirect (complex forming) scattering dynamics and proceeded via the formation of a van-der-Waals complex ($^{11}\text{BOC}_3\text{H}_4$). This complex isomerized via addition of the boron monoxide radical ($^{11}\text{BO}; \text{X}^2\Sigma^+$) with the radical center located at the boron atom to the terminal carbon atom of the allene molecule forming a $\text{H}_2\text{CCCH}_2^{11}\text{BO}$ intermediate on the doublet surface. The chemically activated $\text{H}_2\text{CCCH}_2^{11}\text{BO}$ intermediate underwent unimolecular decomposition via atomic hydrogen elimination from the terminal carbon atom holding the boronyl group through a tight exit transition state to synthesize the boronyllallene product ($\text{H}_2\text{CCCH}^{11}\text{BO}$) in a slightly exoergic reaction ($53 \pm 11 \text{ kJ mol}^{-1}$). Statistical (RRKM) calculations suggest that minor reaction channels lead to the products 3-propynyl-oxo-borane ($\text{CH}_2(^{11}\text{BO})\text{CCH}$) and 1-propynyl-oxo-borane ($\text{CH}_3\text{CC}^{11}\text{BO}$) with fractions of 1.5 % and 0.2 %, respectively. The title reaction was

also compared with the cyano ($\text{CN}; \text{X}^2\Sigma^+$) – allene and boronyl – methylacetylene reactions to probe similarities, but also differences of these isoelectronic systems. Our investigation presents a novel gas phase synthesis and characterization of a hitherto elusive organyl-oxo-borane (RBO) monomer – boronylallene - which are inherently tricky to isolate in the condensed phase except in matrix studies; our work further demonstrates that the crossed molecular beams approach presents a useful tool in investigating the chemistry and synthesis of highly reactive organyl-oxo-boranes.

3.7. Crossed Beam Reaction of Boron Monoxide with Propylene (P12)

The reaction dynamics of boron monoxide ($^{11}\text{BO}; \text{X}^2\Sigma^+$) with propylene ($\text{CH}_3\text{CHCH}_2; \text{X}^1\text{A}'$) were investigated under single collision conditions at a collision energy of $22.5 \pm 1.3 \text{ kJ mol}^{-1}$. The crossed molecular beam investigation combined with *ab initio* electronic structure and statistical (RRKM) calculations reveals that the reaction follows indirect scattering dynamics and proceeds via the barrierless addition of boron monoxide radical with its radical center located at the boron atom. This addition takes place to either the terminal carbon atom (C1) and/or the central carbon atom (C2) of propylene (CH_3CHCH_2) reactant forming $^{11}\text{BOC}_3\text{H}_6$ intermediate(s). The long lived $^{11}\text{BOC}_3\text{H}_6$ doublet intermediate(s) underwent unimolecular decomposition involving at least three competing reaction mechanisms via an atomic hydrogen loss from the vinyl group, an atomic hydrogen loss from the methyl group, and a methyl group elimination to form *cis/trans* 1-propenyl-oxo-borane ($\text{CH}_3\text{CHCH}^{11}\text{BO}$), 3-propenyl-oxo-borane ($\text{CH}_2\text{CHCH}_2^{11}\text{BO}$), and ethenyl-oxo-borane ($\text{CH}_2\text{CH}^{11}\text{BO}$), respectively. Utilizing partially deuterated propylene (CD_3CHCH_2 and CH_3CDCD_2), we reveal that the loss of a vinyl hydrogen atom is the dominant hydrogen elimination pathway ($85 \pm 10\%$) forming *cis/trans* 1-propenyl-oxo-borane ($\text{CH}_3\text{CHCH}^{11}\text{BO}$), compared to the loss of a methyl hydrogen atom ($15 \pm 10\%$) leading to 3-propenyl-oxo-borane ($\text{CH}_2\text{CHCH}_2^{11}\text{BO}$). The branching ratios for an atomic hydrogen loss from the vinyl group, an atomic hydrogen loss from the methyl group, and a methyl group loss are experimentally derived to be $26 \pm 8\% : 5 \pm 3\% : 69 \pm 15\%$, respectively; these data correlate nicely with the branching ratios calculated via RRKM theory of $19\% : 5\% : 75\%$, respectively.

3.8. Crossed Beam Reaction of Boron Monoxide with 1,3-Butadiene (P13)

The crossed molecular beam reactions of the boron monoxide ($^{11}\text{BO}; \text{X}^2\Sigma^+$) radical with 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2; \text{X}^1\text{A}_g$) and its partially deuterated counterparts, D2-1,3-butadiene ($\text{CH}_2\text{CDCDCH}_2; \text{X}^1\text{A}_g$) and D4-1,3-butadiene ($\text{CD}_2\text{CHCHCD}_2; \text{X}^1\text{A}_g$), were investigated under single collision conditions exploiting a crossed molecular beams machine. The experimental data were combined with the state-of-the-art *ab-initio* electronic structure calculations and statistical RRKM calculations to investigate the underlying chemical reaction dynamics and reaction mechanisms computationally. Our investigations revealed that the reaction followed indirect scattering dynamics through the formation of $^{11}\text{BOC}_4\text{H}_6$ doublet radical intermediates via the barrierless addition of the ^{11}BO radical to the terminal carbon atom (C1/C4) and/or the central carbon atom (C2/C3) of 1,3-butadiene. The resulting long lived $^{11}\text{BOC}_4\text{H}_6$ intermediate(s) underwent isomerization and/or unimolecular decomposition involving eventually at least two distinct atomic hydrogen loss pathways to 1,3-butadienyl-1-oxoboranes ($\text{CH}_2\text{CHCHCH}^{11}\text{BO}$) and 1,3-butadienyl-2-oxoboranes ($\text{CH}_2\text{C}^{11}\text{BOCHCH}_2$) in overall exoergic reactions via tight exit transition states. Utilizing partially deuterated D2- and D4-1,3-butadiene, we revealed that the hydrogen loss from the methylene moiety (CH_2) dominated with $70 \pm 10\%$ compared to an atomic hydrogen loss from the methylidyne group (CH) of only $30 \pm 10\%$; this data agrees nicely with the theoretically predicted branching ratio of 80 % versus 19%.

3.9. Review Articles – Chem. Soc. Rev. & Acc. Chem. Res. (P8, P14)

The classification of chemical reactions based on shared characteristics is at the heart of the chemical sciences, and is well exemplified by Langmuir's concept of *isovalency*, in which 'two molecular entities with the same number of valence electrons have similar chemistries'. Within this account we further investigate the ramifications of the *isovalency* of four radicals with the same $X^2\Sigma^+$ electronic structure – cyano (CN), boron monoxide (BO), silicon nitride (SiN), and ethynyl (C_2H), and their reactions with simple prototype hydrocarbons acetylene (C_2H_2) and ethylene (C_2H_4). The fact that these four reactants own the same $X^2\Sigma^+$ electronic ground state should dictate the outcome of their reactions with prototypical hydrocarbons holding a carbon-carbon triple and double bond. However, we find that other factors come into play, namely, atomic radii, bonding orbital overlaps, and preferential location of the radical site. These doublet radical reactions with simple hydrocarbons play significant roles in extreme environments such as the interstellar medium and planetary atmospheres (CN, SiN and C_2H), and combustion flames (C_2H , BO).

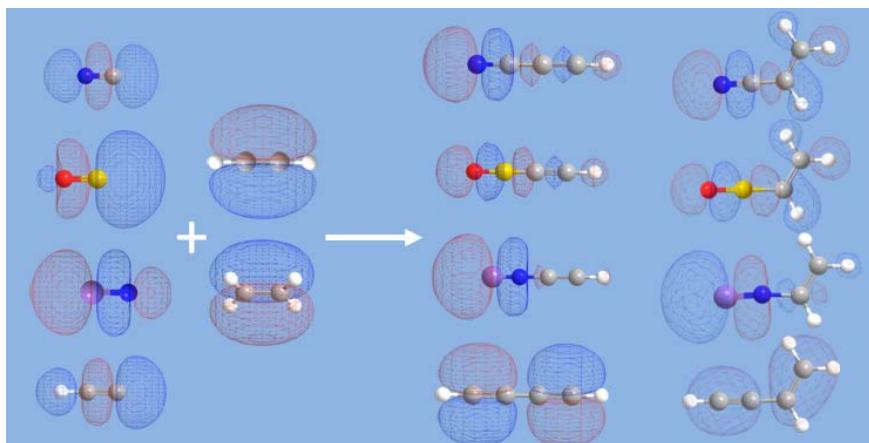


Fig. 1: Reaction products of isoelectronic boron monoxide (BO), cyano (CN), ethynyl (CCH), and silicon nitride (SiN) radicals with acetylene and ethylene.

3.10. Crossed Beam Reaction of Boronylsulfide with Acetylene (P10)

This presents a small add-on project to probe the reaction dynamics of the boronylsulfide radical (BS), which is isoelectronic to the boron monoxide radical (BO). As a member of the organo sulfidoboron (RBS) family, the hitherto elusive ethynylsulfidoboron molecule (HCCBS) has been synthesized for the very first time via the bimolecular reaction of the boron monosulfide radical (BS) with acetylene (C_2H_2) under single collision conditions in the gas phase exploiting the crossed molecular beams technique. The reaction mechanism follows indirect dynamics via a barrierless addition of the boron monosulfide radical with its boron atom to the carbon atom of the acetylene molecule leading to the *trans*-HCCHBS intermediate. The initial collision complex was found to isomerize to its *cis*-form and undergoes a hydrogen migration to form H₂CCBS. The *cis*-HCCHBS intermediate either isomerizes via hydrogen shift from the carbon to the boron atom leading to the HCCBHS isomer or decomposes to ethynylsulfidoboron (HCCBS). Both H₂CCBS and HCCBHS intermediates were found to fragment to ethynylsulfidoboron via atomic hydrogen losses. Statistical (RRKM) calculations report yields to form the ethynylsulfidoboron molecule from *cis*-HCCHBS, H₂CCBS, and HCCBHS to be 21%, 7% and 72%, respectively, under current experimental conditions. Our findings open up an unconventional path to access the previously obscure class of organo sulfidoboron molecules, which are difficult to access through 'classical' synthesis.

3.11. Crossed Beam Reaction of Boronylsulfide with Ethylene (P11)

We exploited crossed molecular beams techniques and electronic structure calculations to provide compelling evidence that the vinylsulfidoboron molecule ($C_2H_3^{11}B^{32}S$) – the simplest member of hitherto elusive olefinic organo-sulfidoboron molecules (RBS) – can be formed via the gas phase reaction of boron monosulfide ($^{11}B^{32}S$) with ethylene (C_2H_4) under single collision conditions. The reaction mechanism follows indirect scattering dynamics via a barrierless addition of the boron monosulfide radical to the carbon-carbon double bond of ethylene. The initial reaction complex can either decompose to vinylsulfidoboron ($C_2H_3^{11}B^{32}S$) via the emission of a hydrogen atom from the sp^3 hybridized carbon atom, or isomerize via a 1,2-hydrogen shift prior to a hydrogen loss from the terminal carbon atom to form vinylsulfidoboron. Statistical (RRKM) calculations predict branching ratios of 8 % and 92 % for both pathways leading to vinylsulfidoboron, respectively. A comparison between the boron monosulfide ($^{11}B^{32}S$) plus ethylene and the boron monoxide (^{11}BO) plus ethylene systems indicate that both reactions follow similar reaction mechanisms involving addition – elimination and addition – hydrogen migration – elimination pathways. Our experimental findings open up a novel pathway to access the previously poorly-characterized class of organo-sulfidoboron molecules via bimolecular gas phase reactions, which are difficult to form through ‘classical’ organic synthesis.

3.12. Higher Order Carbon Sulfides (P2, P3)

This presents a small add-on project to investigate the formation of model compounds of high energy-density molecules and builds up on our previously successful synthesis of higher carbon oxides CO_x ($x=3-6$). Higher-order carbon sulfides - carbon tetrasulfide (CS_4 ; D_{2d}), carbon pentasulfide (CS_5 ; C_2), and carbon hexasulfide (CS_6 , C_2) - were detected for the first time via infrared spectroscopy in low temperature carbon disulfide (CS_2) ices upon irradiation with energetic electrons. The identification of these molecules was aided via observed band positions of their C-12 and C-13 isotopologues and the agreement with vibrational modes and isotope shifts predicted from *ab initio* calculations. In addition to these complex carbon sulfides, we also detected well-known smaller carbon- and sulfur-bearing molecules, namely carbon trisulfide (CS_3 ; C_{2v}), carbon monosulfide (CS , $C_{\infty v}$), dicarbon disulfide (C_2S_2 , $D_{\infty h}$), and carbon subsulfide (C_3S_2 , $D_{\infty h}$). We also attempted to synthesize mixed cyclic oxygen-sulfur-carbon-bearing species, but failed; all sulfur was incorporated solely in sulfur oxides.

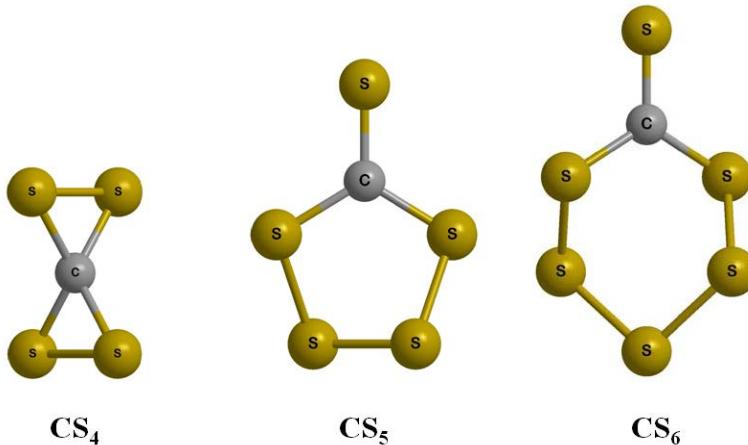


Fig. 2: Newly formed carbon tetrasulfide (CS_4 ; D_{2d}), carbon pentasulfide (CS_5 ; C_2), and carbon hexasulfide (CS_6 , C_2) molecules.

4. Personnel Associated with the Research Effort

During this reporting period, postdoctoral fellows Dr. Pavlo Maksyutenko, Dr. Surajit Maity, and Dr. Beni Dangi were supported on the AFOSR grant. Support was also given to the PI (summer overload). Finally, Edwin Kawamura (Staff Scientist, University of Hawaii) was available for this project to build and to maintain electronic equipment.

5. Publications (4/12 – 4/15)

P1. D.S.N. Parker, F. Zhang, P. Maksyutenko, R. I. Kaiser, *A crossed beam and ab initio investigation of the reaction between boron monoxide ($BO; X^2\Sigma^+$) and ethylene ($C_2H_4; X^1A_g$)*. Physical Chemistry Chemical Physics 14, 11099-11106 (2012).

P2. S. Maity, Y. S. Kim, R.I. Kaiser, H.C.C. Chang, *On the Detection of Higher Order Carbon Sulfides (CS_x ; $x = 4-6$) in Low Temperature Carbon Disulfide Ices*. CPL 577 42-47 (2013).

P3. S. Maity, R.I. Kaiser, *Electron Irradiation of Carbon Disulfide – Oxygen ices: Toward the Formation of Sulfur-Bearing Molecule in the Interstellar Medium*. The Astrophysical Journal 773, 184-193(2013).

P4. D.S.N. Parker, N. Balucani, D. Stranges, R.I. Kaiser, A.M. Mebel, *A Crossed Beam and Ab Initio Investigation on the Formation of Boronyldiacetylene ($HCCCC^{11}BO; X^1\Sigma^+$) via the Reaction of the Boron Monoxide Radical ($^{11}BO; X^2\Sigma^+$) with Diacetylene ($C_4H_2; X^1\Sigma_g^+$)*. The Journal of Physical Chemistry A 117, 8189-8198 (2013).

P5. S. Maity, D.S.N. Parker, B. Dangi, R.I. Kaiser, S. Fau,, S.A. Perera, R.J. Bartlett, *A Crossed Molecular Beam and Ab-Initio Investigation on the Reaction of Boron Monoxide ($BO; X^2\Sigma^+$) with Methylacetylene ($CH_3CCH; X^1A_1$) – Competing Atomic Hydrogen and Methyl Loss Pathways*. The Journal of Physical Chemistry A 117 11794–11807 (2013).

P6. D.S.N. Parker, N. Balucani, D. Stranges A.M. Mebel, R.I. Kaiser, *First Gas Phase Synthesis of Phenylxo-borane (C_6H_5BO) via the Reaction of Boron Monoxide with Benzene*. JOC 78, 11896-11900 (2013).

P7. R.I. Kaiser, S. Maity, B. Dangi, A.H.H. Chang, *A Crossed Molecular Beam and Ab-Initio Investigation of the Exclusive Methyl Loss Pathway in the Gas Phase Reaction of Boron Monoxide ($BO; X^2\Sigma^+$) with Dimethylacetylene ($CH_3CCCH_3; X^1A_{1g}$)*. CCP 16, 989-997 (2014).

P8. D.S.N. Parker, R.I. Kaiser, T. Labrador, A.M. Mebel, *The Role of Isoelectronicity in the Reactions of the Cyano (CN), Boron Monoxide (BO), Silicon Nitride (SiN), and Ethynyl (C_2H) Radicals with Unsaturated Hydrocarbons Acetylene (C_2H_2) and Ethylene (C_2H_4)* Chem. Soc. Rev. 43, 2701-2713 (2014).

P9. S. Maity, D.S.N. Parker, R.I. Kaiser, R.J. Bartlett, *Gas-Phase Synthesis of Boronyllallene ($H_2CCCH(BO)$) under Single Collision Conditions – A Crossed Molecular Beams and Computational Study*. The Journal of Physical Chemistry A 118, 3810-3819 (2014).

P10. T. Yang, D. Parker, D. Stranges, A.H.H. Chang, R.I. Kaiser, *On the Synthesis of the Ethynylsulfidoboron Molecule (HCCBS)*. 136, 8387-8392. The Journal of the American Chemical Society (2014).

P11. T. Yang, B.B. Dangi, D.S.N. Parker, R.I. Kaiser, A.H.H. Chang, *A Combined Crossed Molecular Beams and Ab Initio Investigation on the Formation of Vinylsulfidoboron (C_2H_3BS) -*

The Simplest Olefinic Organosulfidoboron Molecule. Physical Chemistry Chemical Physics 16 17580-17587 (2014).

P12. S. Maity, B.B. Dangi, D.S.N. Parker, R.I. Kaiser, H.C.C. Chang, *A Combined Crossed Molecular Beam and Ab Initio Investigation of the Multichannel Reaction of Boron Monoxide (BO ; $X^2\Sigma^+$) with propylene (CH_3CHCH_2 ; X^1A') – Competing Atomic Hydrogen and Methyl Loss Pathways.* The Journal of Physical Chemistry A 118, 9632-9645 (2014).

P13. S. Maity, B. B. Dangi, D.S.N. Parker, R.I. Kaiser, H.M. Lin, H.P. E, B.J. Sun, A. H. H. Chang, *A Combined Crossed Molecular Beam and Ab-Initio Investigation of the Reaction of Boron Monoxide (BO ; $X^2\Sigma^+$) with 1,3-Butadiene ($CH_2CHCHCH_2$; X^1A_g) and Its Deuterated Counterparts.* The Journal of Physical Chemistry A 119, 1094-1107 (2015).

P14. N. Balucani, R.I. Kaiser, *Untangling the Chemical Dynamics of Boron Monoxide Reactions with Hydrocarbons,* Acc. Chem. Res (submitted 2015).

6. Invention Disclosures and Patents Granted

There is nothing to report here.

7. Honors and Awards

The PI was elected *Fellow of the American Physical Society* (2012), the *American Association for the Advancement of Science (AAAS)* (2013), and of the *Institute of Physics (UK)* (2014)

1.

1. Report Type

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The full title of the funded effort.

Untangling the Energetics and Dynamics of Elementary Reactions of the Boron Monoxide Radical (11BO; X₂Σ+)

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-12-1-0213

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Ralf I. Kaiser

Program Manager

The AFOSR Program Manager currently assigned to the award

Dr. Michael Berman

Reporting Period Start Date

04/15/2012

Reporting Period End Date

04/14/2015

Abstract

The objectives of this project are to experimentally explore the energetics, dynamics, and potential energy surfaces (PESs) of elementary reactions of ground state boron monoxide radicals (11BO; X₂Σ+) with key C₂ to C₆ unsaturated hydrocarbons under single collision conditions utilizing a crossed molecular beams machine. Here, we present data on the reactions of the crossed beam reactions of the boronyl radical with unsaturated C₃ to C₆ hydrocarbons and identify previously unobserved organo boronyl molecules relevant to the combustion of boron-doped fuel.

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Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

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